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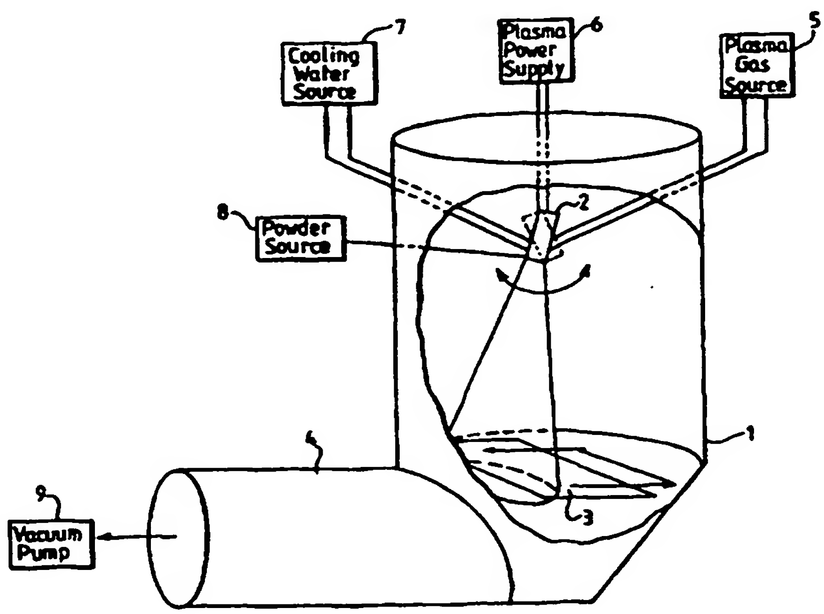

(57) Abstract

The invention relates to an improved method of making a printing plate and an improved printing plate made in accordance with the method. The invention is applicable with particular advantage to the manufacture of plates for use in lithographic printing processes. The method includes the step of depositing upon a substrate (3) a surface layer of particulate material by a plasma spray technique in which the plasma is sprayed onto the substrate into a low pressure environment (1) at a pressure of less than 1.9984 x 10^4Pa (150 torr).

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IMPROVEMENTS IN AND RELATING TO THE MANUFACTURE OF PRINTING PLATES

Field of the Invention

The invention relates to an improved method of making a printing plate and an improved printing plate made in accordance with the method. The invention is applicable with particular advantage to the manufacture of plates for use in lithographic printing processes.

In the specification, the term lithography encompasses any printing process using a printing surface which is essentially planographic and in which the differentiation between the image and the non-printing background is determined by the differences in wettability of the image and background to the printing ink. Typically, the non-image areas are hydrophilic and image areas are generally oleophilic. Consequently, oil based inks are repelled from the non-image areas after water is applied to the plate.

Typically, a lithographic printing plate comprises a substrate including a surface layer upon which an image layer is created. It is created from a printing plate precursor comprising a substrate including a surface layer, upon which a layer of image material is formed. Image and non-image area will be created by exposing the image material to radiation. The exposure to radiation creates solubility differences in the image material of the image and non-image areas. Following development the soluble areas are removed leaving a pattern on the substrate corresponding to the image. This is the completed printing plate ready for use in a process.

Preparation of the substrate base before the image material layer is applied or formed must be such that the material will bond to the base prior to image formation, but allows the release of the soluble image material after development.

Suitable image materials for use in lithographic processes can include those based on diazonium/diazide materials, polymers which undergo depolymerisation or addition photo-polymerisation, and silver halide gelatin assemblies. Examples of suitable materials are disclosed in GB-1592281, GB-A-2031442,GB-A-2069164, GB-A-2080964, GB-A-2109573 and EP-A-377589.

Substrates used in the printing industry commonly comprise an aluminium base layer, which has a layer of aluminium oxide on its surface, intermediate to the base material and a subsequently applied image layer, resulting from a controlled oxidation reaction conducted electrochemically. Prior to the oxidation reaction, the surface of the aluminium base layer is subjected to a cleaning treatment, for example involving washing with alkali. The base layer is then subjected to a texture control treatment, for example involving an etching process, which increases the surface area of the substrate, which in turn controls the strength of the bond between the substrate and the image material and increases the ability of the substrate to hold water. It can be appropriate in some circumstances to modify the characteristics of the surface coating of aluminium oxide in order to ensure that the strength of the bond between the surface and the subsequently applied image layer is appropriate, both in the regions which are to remain bonded to the oxide coating and in the regions which are to be removed. This treatment can involve treatment with water, a solution of a phosphate or silicate salt, or a polycarboxylic acid.

It has been proposed to create a surface layer on a substrate base by a dry deposition technique and, in particular, by plasma spraying. The term "plasma

spraying" will be used to encompass any system which involves the generation of a plasma and the use of its thermal energy to melt solid particles, allowing them to be coated onto a base by simultaneously projecting the plasma and solid particles towards the base. A plasma occurs due to the ionisation of a gas. It should be noted that since ionised particles recombine extremely quickly, it is likely that by the time the spray reaches the base, it will include very high temperature gas particles rather than plasma. The term "plasma" will be used to describe the spray even including recombined gas particles. To initiate ionisation, an external force is needed, which can either be provided by a high temperature or a high-frequency electric field. In an arc plasma process, a high temperature is provided by striking an arc between two electrodes. If the energy of the arc is sufficient, any gas present is ionised and becomes a plasma.

Arc plasma processes for surface coating can be divided into two categories, those using a transferred arc and those using a non-transferred arc. In a non-transferred arc process, an arc is struck between a pair of electrodes with a torch so the gas through which the arc burns is ionised and becomes a plasma. The plasma is then projected beyond the arc (thus beyond the electrodes) towards the surface of the workpiece. In a transferred arc process, the workpiece becomes an electrode and the arc is struck between the torch and the workpiece itself. This requires that the environment between the workpiece and the torch consist of those gases which are to become the plasma.

It has been proposed to form a light sensitive printing plate for use in lithography by creating a surface layer on a substrate base by depositing particulate coating material on the substrate using a plasma spraying technique.

Conventional plasma spraying techniques are carried out at atmospheric pressure.

Although atmospheric plasma spray techniques can be effective in depositing a surface layer on a substrate, a single plasma spray produces a deposit or track of limited width. In the production of lithographic plates, it is desirable to coat substrates of at least 0.5 metre width. The typical track width that can be sprayed at atmospheric pressure is much less than this - of the order of 10 to 20mm when the particle size of the solids prior to melting is between 3 and 5 μm. Making the plasma stream larger in size to increase the area sprayed becomes impractical because of the substantially increased power required to spray over larger areas. This means that in order to cover a large area, a multiplicity of tracks are required. The tracks must be laid down adjacently to cover the whole surface. Thus, to cover a surface, a plurality of plasma spray guns would be required.

A major problem which arises is that no plasma spray gun will be 100% effective. Typically, the percentage of production time during which a viable product can be obtained from one spray gun is 97%. The problem is that as the number of spray units in a system increases, the percentage of time within which viable products can be obtained decreases. Since the capacity of any plasma system will be related not only to the number of guns but to their availability, it can be calculated that the total capacity will actually start to decrease once the number of spray units exceeds a threshold. It has been found that in a system where the percentage availability per unit is 97%, the optimum value is 33 spray units. However, it has been found that this has an overall availability of 37% so that of the time set aside for spraying only 37% produces viable products.

A further problem which arises due to the plurality of tracks is that it is very difficult to produce even spraying since there is a danger of either a gap between adjacent tracks or the tracks overlapping too much or too little. If the tracks overlap too much, a thicker coating may be produced at that point. This can cause problems in the production of lithographic printing plates where accuracy and reliability are required.

Moreover, the plasma and associated molten particles have a heating effect on the base material which has a tendency to soften and warp the base material which means that the plate produced would have a low ultimate tensile strength.

Low pressure and vacuum pressure plasma spraying techniques, ie spraying in a low pressure environment have been developed for special applications, and have been known for over 20 years. Such systems, can be used for example, when covering a particular workpiece requiring a thick coating of dense material or where the coating is one susceptible to oxidation and it is important that no oxidation occurs. The driving force for its introduction was the need by the aerospace industry for high quality coatings on gas turbine parts. By carrying out the plasma spraying in a chamber filled with inert gas at a low pressure, entrainment of air into the plasma spray can be eliminated.

Examples of plasma systems that spray at low pressure are described US patents 3 839 618 and 4 328 257. The processes described are those developed for spraying small workpieces to achieve extremely dense coatings of high purity material. Because the spraying takes place within an enclosed low pressure environment, the size of the workpiece is limited.

Summary of the Invention

According to a first aspect of the invention, there is provided a method of manufacturing a lithographic printing plate precursor, including the step of depositing upon a substrate a surface layer of particulate material by a plasma spray technique in which the plasma is sprayed onto the substrate into a low pressure environment at a pressure of less than 1.9984×10^4Pa (150 torr).

In the foregoing paragraph and the rest of the specification, the term 'substrate' will be used to encompass any surface upon which a particulate material is to be

deposited during the method, and is not limited to the conventional meaning of substrate recognised in lithography ie the surface upon which the light sensitive material is to be coated.

According to a second aspect of the invention, there is provided a lithographic printing plate precursor made in accordance with the method according to the first aspect of the invention.

The third and fourth aspects of the invention relate respectively to a method of manufacturing a lithographic printing plate, and a lithographic printing plate made from that method, in which the printing plate precursor is in accordance with the second aspect of the invention.

Thus, the plasma spraying is carried out at a low pressure compared to atmospheric pressure (1.01325×10^5Pa (760 torr)). The use of low pressure plasma spraying technique has a number of advantages. The first is that it produces a broad plasma stream in order to form a relatively uniform coating on the substrate. With a particular nozzle, for example, that described in copending US application 08/292,399 in the name of EPI, the effect is to produce a large pressure difference between the inside and the outside of the plasma gun used to create the plasma stream which creates a substantial shock pattern as the plasma stream comprising a mixture of gas and material being sprayed exits the plasma gun and travels to the substrate. The plasma stream quickly expands as it exits the plasma gun so as to form a large broad plume pattern particularly at substantial distances from the plasma gun.

The track width is greater than 200mm. This gives increased capacity from a single unit, less spray units are required to approach target production capacity and there is therefore higher overall system availability with less unexpected downtime.

At the same time, such plasma stream has the requisite energy to deposit uniform dense coatings on the substrate at distances which are considerably greater than those normally used in conventional plasma spraying applications. The pressure differential leads to an increase in velocity of the exhaust plasma gases and a length of plasma which is much longer than in atmospheric plasma spraying.

The result of this is that if the distance from the gun to the workpiece and rate of powder feed to the plasma are varied to take into account the increase in plasma length and volume, the width of a deposited coated track from a single gun moving at a particular speed relative to a surface is related to the ambient pressure of the environment in which spraying is performed. Thus different widths of the surface to be sprayed, sometimes known as a web, can be accommodated by specifying particular conditions of powder feed rate, pressure, gun-workpiece distance and the speed of traverse of the gun relative to the web.

Continuous operation can be provided by continuously feeding a web through the pressure chamber in which spraying takes place. The web enters and exits the chamber through one or more seals which, if the vacuum pumps are correctly specified, permit the required operating pressure to be maintained within the chamber. In this case the speed of the gun(s) relative to the web is provided by the speed at which the web moves through the chamber. The guns are positioned to spray onto the web while it is inside the chamber.

Because the distance between the plasma gun and the plate has been increased, the plates produced retain their stiffness, do not warp and have ultimate tensile strength to values above the specified limit for printing plates. This is because at atmospheric pressure the substrate is predominantly heated by a combination of molten particles and plasma in a concentrated area. At low pressure the substrate is predominantly heated by the thermal energy of the molten particles, and any heat input is over a larger area of aluminium which eliminates the need for a

cooling process while spraying and in fact permits the use of a heating process before and during spraying to promote adhesion between the deposited coating and the base material potentially improving characteristics such as bend resistance and chemical resistance.

It has been stated that Low Pressure Plasma Spraying can be used to obtain plasma spray streams with widths well in excess of those produced using atmospheric plasma spraying. The width of the stream produced depends on nozzle design and the pressure differential between the gun and the operating environment. By appropriate selection of these two parameters a system might be produced where the spray issuing from a single gun would be broad enough to cover a base material 1.6m wide.

The following information is based on a particular arrangement, namely an EPI Low Pressure Plasma Spraying system using an EPI-03 plasma gun and a diverging nozzle with a throat diameter of 12.5mm and an exit diameter of 19mm.

Preferably, the pressure of the environment during spraying will be less than 2.6664×10^3Pa (20 torr) but greater than 1.3332 Pa (0.01 torr). More preferably, the pressure will be between 3.9996×10^2Pa and 6.666×10^2Pa (3-5 torr). The pressure within the plasma gun will typically be greater than 5.3329×10^4Pa (400 torr).

Preferably, the distance from the exit of the plasma gun to the surface of the base material will be greater than 200mm, more preferably around 1300mm.

The arc used to generate the plasma is provided by a power supply or a combination of power supplies operating at a particular current and voltage giving a plasma arc having a power greater than 40 kW. Preferably, the power is greater than 92 kW, more particularly between 110 and 120 kW.

The relative speed of the gun to the web can vary from just over $0ms^{-1}$ but is preferably between 0.2 and 0.8 ms^{-1}. As explained the gun or guns may move over the surface of the substrate or the substrate may be in the form of a moving web with stationary guns.

The gas used to generate the plasma preferably consists of a mixture of primary and secondary gases. In one given example, the primary gas is Argon and has a volumetric flow rate of between 30 and 200 litres per minute at standard temperature and pressure (ie standard litres) preferably between 60 and 140 standard litres per minute. The secondary gas may be Helium, Hydrogen or Nitrogen having a flow rate which is preferably greater than 3 standard litres per minutes and usually between 8 and 24 standard litres per minute but less than 40 standard litres per minute. The powder type used is a metallic or ceramic powder, preferably ceramic. Preferably, the ceramic powder will comprise alumina.

The particle size of the powder is preferably less than 20 μm, more preferably less than 12 μm, particularly between 3 and 10 μm.

Each gun can be fed by a number of powder feed units, each unit using a flow of carrier gas to feed a certain mass flow rate of powder to the gun. Preferably, there are a plurality of powder feed units attached to a gun.

Within each powder feed unit, the gas used to carry the powder from the powder feed unit can have a volumetric flow rate greater than 5 standard litres per minute, preferably greater than 10 standard litres per minute, particularly around 20 standard litres per minute. The mass flow rate of powder fed into each carrier gas stream will be at least 10gm per minute, preferably 30gm per minute.

The gas used to carry the powder may be Argon.

Using a single plasma gun capable of handling 120 kW power (compared to 40 kW in an atmospheric system) and operating in a chamber where a long spray distance can be realised (1300mm), a deposited track with a width of 300mm can be obtained the gun moves at a speed of 0.5m/s relative to the surface to be sprayed. The weight of the deposited coating in the latter case can be controlled within a range of 2-10g/m^2, which contains the weight range of an anodic film produced by conventional electrochemical means. These results are based on a single gun, not on a whole system. This result has the following implications:

The potential capacity from a single gun using this method is 540 m^2/hr, more than 5 times that available by pushing atmospheric plasma spraying (100m^2/hr) to its limits (a 10mm track deposited at 3m/s).

A multi-unit system using Low Pressure Plasma Spraying as a basis would need only 3 guns to give a yearly coated output of 10 million m^2, compared to the 33 needed using atmospheric plasma spraying which only attains the maximum production figure of 9 million m^2/yr.

The overall system availability of a 3 unit system is 91% (disregarding possible failures within the vacuum pumping system) compared to the figure of 37% obtained using a 33 gun atmospheric system.

Brief Description of the Drawings

Examples of methods of producing lithographic printing plates in accordance with the invention will now be described with reference to the accompanying drawing and tables in which:-

The Drawing is a schematic view of the apparatus;

Table 1 sets out the conditions used in Example 1;

Table 2 sets out the alterations to Table 1 used in Example 3;

Table 3 sets out further alterations to Table 1 used in Example 4, and

Table 4 sets out the conditions used in Example 5.

Description of the Preferred Embodiment

Examples of substrate produced by Low Pressure Plasma Spraying at EPI (now Sulzer-Metco Irvine) are given hereinafter. The apparatus with which the examples were produced is first briefly described with reference to the accompanying drawing:

The chamber in which spraying takes place (1) is a pressure vessel, connected to a vacuum pump (9) through an arrangement (4) which may include a baffle filter module, a heat exchanger and an overspray filter collector. The vacuum pump is operated to reduce the ambient pressure within the chamber from atmospheric to the desired level.

The sample to be coated (3) is cut into a rectangular section and mounted on a backing plate toward the bottom of the chamber a certain vertical distance below the plasma torch (2). The torch can be oscillated around a fixed centre of rotation. The angular velocity of the torch controls the linear speed at which the spray traverses the workpiece. A single pass occurs when the spray has wholly traversed the workpiece. After each pass, the torch can be manipulated such that the spray moves a certain horizontal distance, or raster step, perpendicular to the direction of traverse.

In order for the plasma spray to be generated the torch must be connected to various feed units. The plasma power supply (6) provides the electrical power required to strike the arc within the plasma torch. The plasma gas source (5) provides the various primary and secondary gases required to form the plasma. The cooling water source (7) is necessary to prevent the heat generated in the plasma from destroying the plasma torch. A powder source (8) consisting of a dehydrated powder and a carrier gas, is necessary to introduce the coating material into the plasma spray. More than one powder source per torch can be used. In the following examples, standard EPI apparatus is used, the torch being an EPI-03 type fitted with a divergent nozzle having a 13mm throat diameter and a 19mm exit diameter.

Example 1

A substrate for use as a lithographic printing plate was made by using the apparatus described above to spray $A1_20_3$ powder on a 0.3mm gauge aluminium alloy sheet of designation AA1050. The $A1_20_3$ powder was supplied by Abrasive Developments Ltd with the designation F1000/5 and a mean particle size of 4.5 μm. It was necessary to dehydrate the $A1_20_3$ powder by preheating in an oven at 200°C for 24 hours prior to spraying. The sheet was cut to size (711mm x 457mm) before mounting on the backing plate.

Table 1 gives the conditions used to spray the $A1_20_3$ powder onto the sheet.

The substrate was used to produce a printing plate by bar coating in the laboratory with a light sensitive material of the type which is applied by Horsell Graphic Industries Limited to light sensitive lithographic printing plates sold by them under the trade mark CAPRICORN at a coating weight of $2g/m^2$.

Table 1

Primary plasma gas	Argon
Secondary plasma gas	Hydrogen
Primary gas flow	80l.min^{-1} (@ s.t.p.)
Secondary gas flow	10l.min^{-1} (@ s.t.p.)
Arc current	2100A
No. of powder feed units	2
Powder unit disc speed	10%
Powder unit carrier gas flow	2l.min^{-1} (@ s.t.p.)
Chamber pressure	3 torr
Torch-workpiece distance	1350mm
Linear spray speed	0.4m.s^{-1}
Raster step size	200mm
Passes/raster	1

Example 2

A substrate for use as a printing plate was produced using similar conditions to those given in example 1, but using a sheet of aluminium alloy AA3104 which had been treated by (i) dipping in a 5% w/w solution of NaOH and (ii) dipping in a 7% w/w solution of HNO_3.

A printing plate was made from the substrate using the technique described in Example 1.

Example 3

A substrate for use as a printing plate was produced using similar conditions to those given in example 1, apart from the alterations in Table 2.

Table 2

No of powder feed units	4
Linear spray speed	$0.8 m.s^{-1}$

A printing plate was made from the substrate using the technique described in example 1.

Example 4

A substrate for use as a printing plate was produced using similar conditions to those given in example 1, but using $A1_20_3$ powder supplied by Abrasive Developments Ltd with the designation F600/9 and a mean particle size of

9.3 μm. In addition, further alterations were made, shown in Table 3.

Primary gas flow	$118 l.min^{-1}$ (@ s.t.p.)
Secondary gas flow	$8 l.min^{-1}$ (@ s.t.p.)
Arc current	1800A

Table 3

A printing plate was made from the substrate using the technique described in example 1.

Example 5

A substrate for use as a lithographic printing plate was made by using the apparatus described above to spray. $A1_2O_3$ powder onto a 0.3mm gauge aluminium alloy sheet of designation AA1050. The $A1_20_3$ powder was supplied by Fulton Abrasive Systems Inc with the description 800 mesh and had a mean particles size of 7 μm. It is necessary to dehydrate the powder by preheating in an oven at 200°C for 24 hours prior to spraying. The sheet was cut to size (711mmx457mm) before mounting on the backing plate.

Table 4 gives the conditions used to spray the $A1_2O_3$ powder onto the sheet.

Table 4

Primary plasma gas	Argon
Secondary plasma gas	Hydrogen
Primary gas flow	$118l.min^{-1}$ (@ stp)
Secondary gas flow	$14l.min^{-1}$(@ stp)
Arc current	2400A
No. of powder feed units	4
Powder unit disc speed	7%
Powder unit carrier gas flow	$23l.min^{-1}$ (@ stp)
Chamber pressure	2 torr
Torch-workpiece distance	1350 mm
Linear spray speed	$0.8m.s^{-1}$
Raster step size	200mm
Passes/raster	1

The substrate was used to produce a printing plate by bar coating in the laboratory with a light sensitive material of the type which is applied by Horsell Graphic Industries Limited to light sensitive lithographic printing plates sold by them under the trademark CAPRICORN at a coating weight of $2g/m^2$.

Example 6

A substrate for use as a printing plate was produced using similar conditions to those given in example 5, but using a sheet of aluminium alloy AA3104 which had been treated by dipping in a 5% w/w solution of NaOH.

A printing plate was made from the substrate using the technique described in Example 5.

CLAIMS

1 A method of manufacturing a lithographic printing plate precursor, including the step of depositing upon a substate a surface layer of particulate material by a plasma spray technique in which the plasma is sprayed onto the substrate into a low pressure environment at a pressure of less than 1.9984×10^4 Pa (150 torr).

2 A method according to claim 1 in which the pressure of the environment during spraying is between 1.3332 Pa (0.01 torr) and 2.6664×10^3 Pa (20 torr).

3 A method in accordance with claim1 in which the pressure of the environment during spraying is between 3.9996×10^2 Pa and 6.666×10^2 Pa (3 to 5 torr).

4 A method in accordance with any one of the preceding claims in which the distance between a plasma gun producing the plasma and the substrate is greater than 200 millimetres.

5 A method according to claim 4 in which the distance from the exit of the plasma gun to the substrate is around 1300 millimetres.

6 A method in accordance with any one of the preceding claims in which the plasma arc has a power greater than 92 kW.

7 A method according to claim 6 in which the power of the plasma arc is between 110 and 120 kW.

8 A method according to any one of the preceding claims in which the gas used to generate the plasma comprises a mixture of primary and secondary gases.

9 A method in accordance with claim 8 in which the primary gas is Argon, having a volumetric flow of between 60 and 140 standard litres per minute.

10 A method in accordance with claim 8 or 9 in which the secondary gas is one of Helium, Hydrogen and Nitrogen, having a flow rate between 3 and 40 standard litres per minute.

11 A method in accordance with claim 10 in which the flow rate of the secondary gas is between 8 and 24 standard litres per minute.

12 A method in accordance with any one of the preceding claims in which the particulate material is a ceramic powder.

13 A method in accordance with claim 12 in which the ceramic powder comprises alumina.

14 A method in accordance with any one of the preceding claims in which the particle size of the particulate material is less than 20 μm.

15 A method in accordance with claim 14 in which the particle size is less than 12 μm.

16 A method in accordance with claim 15 in which the particle size is between 3 and 10 μm.

17 A method in accordance with any one of the preceding claims in which the plasma gun producing the plasma has a plurality of powder feed units attached thereto, to feed the particulate material.

18 A method in accordance with claim 17 in which the volumetric flow rate of the powder feed unit is greater than 5 standard litres per minute.

19 A method in accordance with claim 17 in which the powder feed unit has a volumetric flow rate of greater than 10 standard litres per minute.

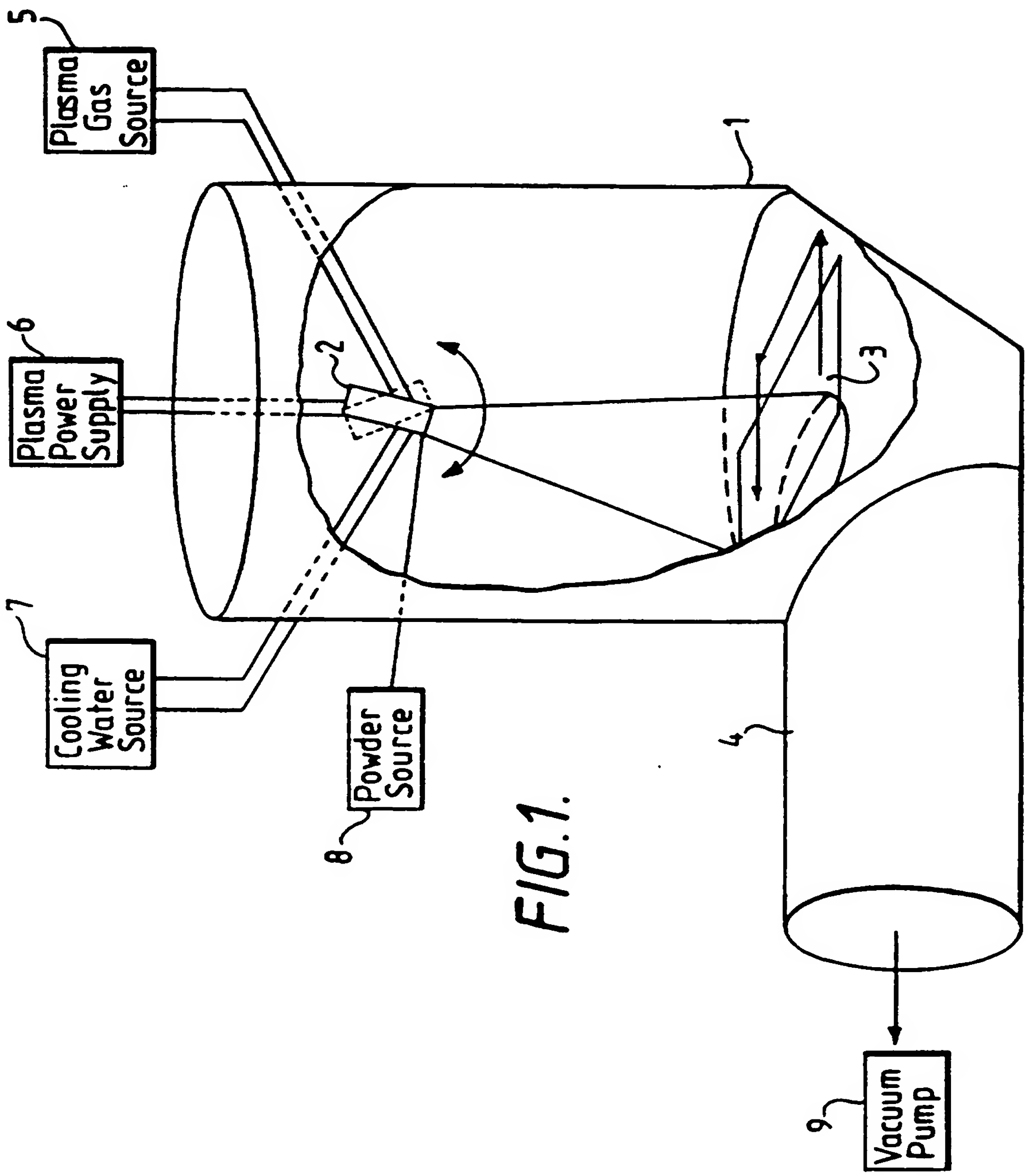
20 A method in accordance with claim 18 in which the volumetric flow rate of the powder feed unit is in the region of 20 standard litres per minute.

21 A method in accordance with any one of the preceding claims in which a plurality of plasma guns produce plasma sprayed onto the substrate.

22 A lithographic printing plate precursor, including a substrate and a surface layer of particulate material, deposited upon the substrate by a plasma spray technique in which the plasma is sprayed onto the substrate into a low pressure environment at a pressure of less than 1.9984×10^4 Pa (150 torr).

23 A method of manufacturing a lithographic printing plate in which the printing plate precursor is manufactured in accordance with claim 1.

24 A lithographic printing plate which has been made from a printing plate precursor in accordance with claim 22.


Plasma Gas Source
Plasma Power Supply
Cooling Water Source
Powder Source
Vacuum Pump
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4
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6
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8
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FIG.1.

INTERNATIONAL SEARCH REPORT

Intern. ...nal Application No
PCT/GB 95/01960

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C4/12 B41N3/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C23C B41N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A,94 05507 (HORSELL GRAPHIC INDUSTRIES) 17 March 1994	1
A	see claims 1-25	12-16, 22-24

Y	WT ZEITSCHRIFT FUR INDUSTRIELE FERTIGUNG, vol. 67, 1977 MUCHEN,DE, pages 321-325, R. SCHARWACHTER 'technik und anwendung des plasmaspritzen im vakuum'	1
A	see page 321 - page 325	4,8,12, 14,17

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search	Date of mailing of the international search report
4 December 1995	15. 12. 95

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